PRE-MELTING MODE IN THE DISORDERED KNO_3 CRYSTAL OBSERVED BY THE LOW-FREQUENCY RAMAN SCATTERING

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On heating, potassium nitrate, KNO_3 undergoes a structural phase transition from the orthorhombic structure (phase II) to the trigonal structure (phase I) at 403 K(T_c) and melts at 606 K(T_m). The central peak in low-frequency Raman scattering spectra of KNO_3 was studied from room temperature up to 130 K above the melting point T_m. A drastic growth was observed with increasing temperature below and above T_m. The spectra were numerically analyzed and the results revealed that the central peak of KNO_3 consists of two spectral components; one is common between the solid state phase I and the molten state, and the other is sensitive for melting process.

Experiment

A single crystal of KNO_3 was grown from aqueous solution. The crystal axes were determined from the crystal habit. After cut and polished, the specimen was placed in the scattering

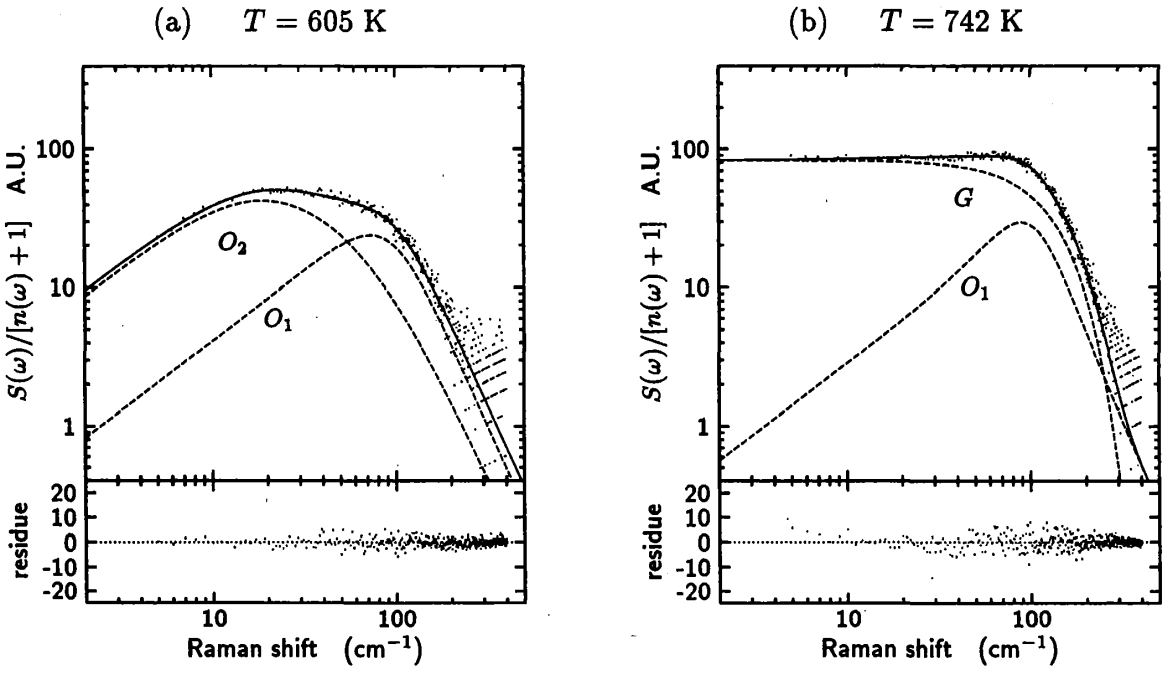

Figure 1: Numerical fit of the central peak of KNO_3 in the solid state phase I (a), and in the molten state (b). Upper figures, dots are observed spectra corrected by Bose-Einstein thermal factor $n(\omega) + 1$. (a) Two damped-harmonic oscillator functions, $O_i = A_i \omega_i^2 \Gamma_i \omega / \left[(\omega_i^2 - \omega^2)^2 + \Gamma_i^2 \omega^2\right], i = 1, 2$. (b) One damped-harmonic oscillator function O_1 and a Gaussian function $G = A_g \exp(-a_g \omega^2)$. Lower figures indicate the residue of the fit.

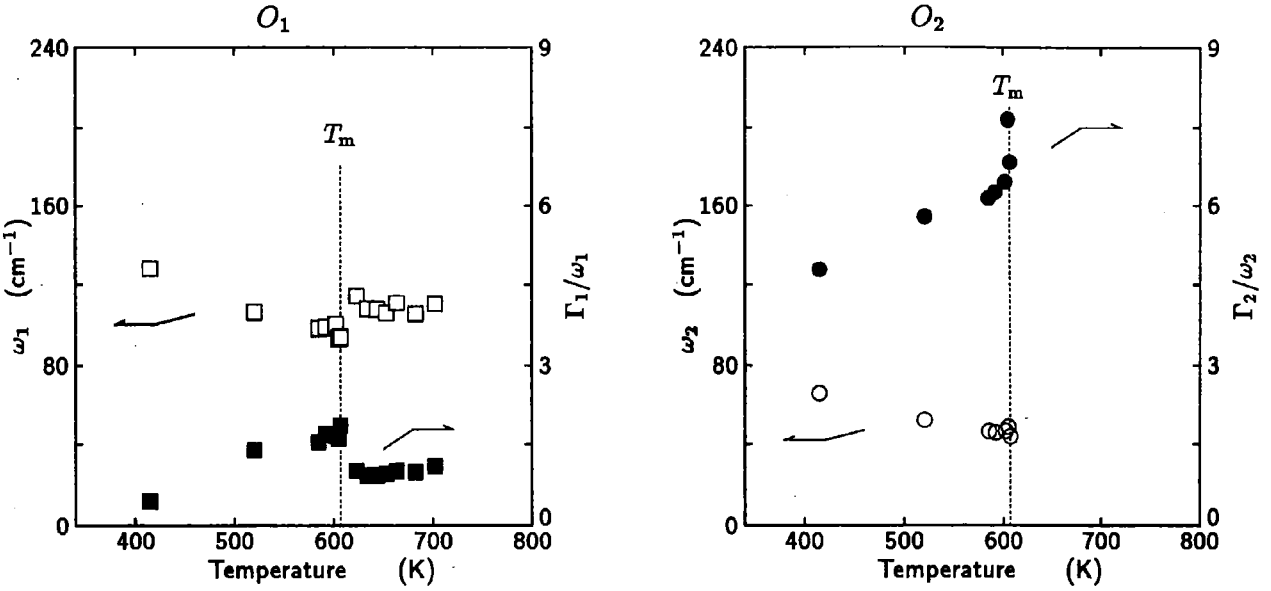

Figure 2: Temperature dependece of the components O_1 and O_2 obtained from numerical analysis.

cell with a temperature controller. An Ar^+ ion laser was used as light source with 514.5 nm at 100 mW. The light scattered at 90 degree from the specimen was analyzed with an 80 cm double monochromater.

The low-frequency Raman spectra were observed in $a(cc)b$,$a(ca)b$,$a(ba)b$ and $a(bc)b$ geometries, which is denoted by the orthorhombic (phase II) axes. The spectra shows good agreement with previous studies.[1,2] The central peak, in any geometry, shows drastic growth with increasing temperature. In particular, the polarized central peak grows extremely in the $a(cc)b$ geometry.

Numerical Analysis

We tried to fit the observed spectra using several functions. As shown in Figure 1, the best fit was obtained for the spectra in solid state phase I with a set of two damped-harmonic oscillator functions ($O_i = A_i \omega_i^2 \Gamma_i \omega / \left[(\omega_i^2 - \omega^2)^2 + \Gamma_i^2 \omega^2\right], i = 1,2$), and for the spectra in molten state with a set of a Gaussian function ($G = A_g \exp(-a_g \omega^2)$) and a damped-harmonic oscillator function(O_1).[3,4]

Temperature dependence of the damped harmonic oscillator functions O_i is shown in Figure 2. The componet O_1 is characteristic of the molten state even in the solid state, or it exists as a common mode. The other one O_2 becomes instable near T_m, which indicates the relation to the melting process, thus it should be termed as a melting mode in the solid state. These modes should be coupled with each other in the solid state, because of the similar temperature dependence of frequency.

References

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